

## DESIGNED COAL LIQUEFACTION CATALYSTS

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### ABSTRACT

The effects and ramifications of using highly dispersed catalysts for coal liquefaction are discussed. We have briefly explored several types of iron and molybdenum based complexes as precursors to high dispersion catalysts. The precursors were either organometallic complexes or water soluble salts and were impregnated into coals of various ranks. The molybdenum catalysts were found to be very effective for an Illinois #6 bituminous coal whereas the iron catalysts were not. In contrast, the iron catalysts were found to be very effective for lignite conversions. Both a H-donor conversion system and a non-donor system were compared, using tetralin and n-hexadecane, respectively. In each case the organometallic precursor gave greater yields of toluene soluble material, with differences being most dramatic in the hexadecane system. The yields using the organometallic molybdenum precursors in hexadecane were found to be almost as great as those in the tetralin system, indicating that with a good enough catalyst precursor, donor solvents are not needed.

### INTRODUCTION

One of the keys to a successful coal liquefaction process is the control of preconversion reactions. Coal is composed of numerous functional groups and classes of molecules. Depending on reaction conditions, these groups may either undergo polymerization and char formation, or bond breaking reactions to form gases and coal liquids. These reactions may occur at quite low temperatures, and thus finding appropriate process conditions and reactive catalysts to control these reactions is critical. For instance, several workers have shown that phenolics tend to polymerize into difficult to upgrade materials unless treated by some means such as a donor solvent such as tetralin (1,2). Current liquefaction processes have shown the benefits of staging the severity of the liquefaction process in order to control preconversion reactions, but are limited in choices of catalyst. Supported catalysts are often used for these processes but suffer in that they only interact with the liquefaction solvent, and have very poor intimate contact with the individual coal molecules. The function of these supported catalysts is primarily to transfer hydrogen to the liquefaction solvent. A more efficient process would involve highly dispersed catalysts that have intimate contact with the coal molecules, have high surface areas or are soluble so that only small amounts of catalyst are needed, and most importantly, would be active at preconversion conditions to limit the amount of retrogressive reactions that occur in the initial stages of coal liquefaction.

Generally, efforts to use dispersed catalysts during coal liquefaction utilize precursors that are not activated until high temperatures (3-6). For instance, molybdenum is often added as either the oxide, the thiolate water soluble salt, or as molybdenum naphthenate, so the molybdenum must first be transformed from the oxide to the trisulfide, and finally transformed to the disulfide, the most active form of the catalyst. However, the conversion of the trisulfide to disulfide occurs only under high temperatures, in excess of 350°C (7). Likewise, a commonly used iron precursor, iron oxide, is difficult to convert to the active pyrrhotite and requires high temperature activation. A soluble organometallic precursor, iron carbonyl has also been investigated; however, it likewise is difficult to activate and tends to form iron carbides and oxides during the activation process (6).

In recent work we have investigated precursors designed to have the correct stoichiometry of the active catalyst (8-10). These precursors can form high surface area catalysts that are active at low temperatures, and thus may limit the polymerization or retrogressive reactions that occur during coal preconversion. The following work describes our efforts to study the reactivities and effects of these types of catalysts for coal liquefaction. Our goals are to synthesize and test soluble complexes that are as close to the correct stoichiometry and structure of the active catalyst during the coal liquefaction. Thus we hope that our catalysts, since they do not require high temperature activation, will cause bond breaking reactions at lower temperatures than are currently possible with dispersed catalysts, and may therefore aid in reducing retrogressive reactions.

## EXPERIMENTAL

The coals used were PSOC 1098 Illinois #6 and Beulah-Zap North Dakota lignite from the Argonne coal bank. The ratio of catalyst to coal was approximately 0.6 mmoles of metal per gram of coal. The organometallic molybdenum catalyst was  $\text{Cp}_2\text{Mo}_2(\mu\text{-SH})_2(\mu\text{-S})_2$ , referred to as  $\text{MoS}_2(\text{OM})$ , and was prepared by modification of method of Dubois et al. (11). Pentacarbonyl iron was obtained from Aldrich, and the sulfur-containing iron cluster,  $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$  was prepared by the method of Bogan et al. (12). Ammonium tetrathiomolybdate,  $\text{MoS}_4(\text{Aq})$ , was obtained from Alfa Chemicals. The organometallic catalysts were impregnated into the coal in tetrahydrofuran (THF) with the exception of the iron complexes, where the reaction solvent was used. The THF was removed by evaporation under vacuum at room temperature. The molybdenum salt was added as an aqueous solution. The coal liquefaction experiments were conducted in a 300 mL Autoclave Engineers stirred reactor using 5.0 g of coal, 30 g of liquefaction solvent, and 500 psig hydrogen. Temperatures of either 400°C or 425°C for 20 minutes using either tetralin or n-hexadecane were used for these conversions. After the reaction had cooled, the coal liquid and residue were taken up in THF. The THF was removed under reduced pressure and the residue taken up in toluene. The product was filtered through a medium porosity filter and separated into toluene soluble (TS) and insoluble (TI) fractions. The toluene and residual tetralin, if used, were then removed from the TS under reduced pressure. The TS and TI fractions were then dried at 76°C for 12 h under vacuum (< 0.1 mm). The conversions were calculated from the amount of toluene-insoluble material and are based on daf basis, or the carbon balance, as in the case of the lignite.

## RESULTS AND DISCUSSION

Data from coal conversions in tetralin and hexadecane solvent systems are presented in Tables 1 and 2, respectively. The Illinois #6 coal gave quite high conversions to toluene soluble material even under the mild conditions of 500 psig hydrogen pressures and 400°C when tetralin was used for the coal liquefaction, as expected for a high volatile bituminous coal. Also as expected, it gave poor conversions in the absence of catalyst in the non-donor hexadecane solvent. The tetralin appeared to moderate the effects of the catalysts, so that the range of conversions was only about 13%. For example, the conversion to toluene soluble material in the absence of catalyst in tetralin was 48%,

compared to 53% when impregnated with aqueous molybdenum, and 61% the coal was impregnated with organometallic molybdenum. A similar range was observed with the conversion temperature increased to 425°C. The iron catalyzed reactions, utilizing  $\text{Fe}(\text{CO})_5$  and the iron sulfido dimer,  $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ , designated as  $\text{Fe}_2\text{S}_2$  showed no apparent effect from the non-catalyzed conversions. However, the TS product of the  $\text{Fe}_2\text{S}_2$  catalyst was a tar while the product from the  $\text{Fe}(\text{CO})_5$  catalyzed reaction was a brittle solid. Experiments with model compounds have shown that the  $\text{Fe}(\text{CO})_5$  tends to form tars as well as metal carbides and oxides, whereas the  $[\text{SFe}(\text{CO})_3]_2$  shows no evidence of polymerization reactions or other products besides iron sulfides, and we suggest that further investigation of these products will show that the latter gives a better quality product.

The oxygen content of the TS product of the catalyzed conversions were found to be lower than those of the non-catalyzed runs. For instance, the molybdenum catalyzed reactions had the lowest oxygen content of 4.6 to 4.8% oxygen, the iron catalyzed reactions gave a 5% oxygen content, and the base line runs an oxygen content of 6-6.5%. The lower oxygen content is one of the goals of our work, since many of the retrogressive reactions are thought to center through this group. In future work we hope to determine whether the reduction of oxygen occurs during the preconversion reactions as we speculate, or during the more severe reactions during coal conversion.

Table 2 lists conversions in hexadecane. The use of hexadecane rather than a typical conversion medium was induced by the desire to use a non-reacting, non-donor conversion medium that would not interfere with the study of the catalysts. As shown in the table, most of the conversions are quite low, as expected. For instance in the absence of catalyst the Illinois #6 coal was converted to 25% toluene soluble material, compared to 48% in tetralin. However, in the presence of the molybdenum catalysts, the conversions were greatly enhanced. For instance, the aqueous molybdenum impregnation gave a conversion of 41% and the organometallic molybdenum impregnation resulted in a conversion of 54%, which is nearly as great as when tetralin was used as the conversion medium. The iron catalyzed conversions showed little effect from the non-catalyzed runs for the Illinois #6 coal; however, showed a significant improvement for the conversion of lignite, with conversions of approximately 40% toluene soluble compared to 24% with no catalyst. Thus the iron complexes appear to be best suited towards low rank coals, presumably due to their increased oxygen functionalities. The  $\text{Fe}_2\text{S}_2$  catalyst appears to have slightly more asphaltenes in the product distribution, but future work will be needed to further study any differences in reactivities between these catalysts.

## CONCLUSIONS

Dispersed catalytic liquefaction has several distinct advantages over conventional thermal or catalytic liquefaction. In the presence of hydrogen, a suitably dispersed catalyst can provide a highly reducing environment within the coal matrix, thus eliminating the need for a good hydrogen donating solvent. An added advantage to these catalysts is that they can promote certain bond cleavage reactions during the liquefaction step. If they can aid in removing the heteroatoms, namely oxygen and nitrogen, during the early stages in coal liquefaction, then the detrimental retrogressive reactions would be minimized. Thus a better quality coal liquid product would be produced that would be easier and less expensive to hydrotreat. The high activity of the molybdenum sulfido complex, we believe, is because the catalyst was impregnated in a highly active form, and thus does not require subsequent activation during the liquefaction step, and thus is active during the preconversion reactions preventing retrogressive reactions. The organometallic iron complexes were found to be effective for low rank coals, and in future work we hope to understand their role in liquefaction in order to better design a more effective liquefaction catalyst.

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Table 1  
Conversion to Toluene Soluble Products in Tetralin<sup>a</sup>

Catalyst	T (°C)	% TS	% O
None	400	48	6.0
MoS <sub>4</sub> (Aq)	400	53	4.8
MoS <sub>2</sub> (OM) <sup>b</sup>	400	61	4.6
Fe(CO) <sub>5</sub>	400	47	5.0
Fe <sub>2</sub> S <sub>2</sub>	400	49	5.1
None	425	69	4.0
MoS <sub>2</sub> (OM) <sup>b</sup>	425	84	2.3
MoS <sub>4</sub> (Aq)	425	76	4.0

<sup>a</sup>Reaction conducted in 300-mL autoclave with 5 g Illinois #6 coal in 30 g solvent and 500 psi H<sub>2</sub> at for 20 min.

<sup>b</sup>OM refers to organometallic precursor.

Table 2  
Conversion to Toluene Soluble Products in Hexadecane<sup>a</sup>

Catalyst	Coal	T (°C)	% TS
None	Ill. # 6	400	25
Fe(CO) <sub>5</sub>	Ill. # 6	400	24
Fe <sub>2</sub> S <sub>2</sub>	Ill. # 6	400	29
MoS <sub>4</sub> (Aq)	Ill. # 6	400	41
MoS <sub>2</sub> (OM)	Ill. # 6	400	54
None	Lignite	425	24
Fe(CO) <sub>5</sub>	Lignite	425	41
Fe <sub>2</sub> S <sub>2</sub>	Lignite	425	39

<sup>a</sup>Reaction conducted in 300-mL autoclave with 5 g coal in 30 g solvent and 500 psi H<sub>2</sub> at for 20 min.

<sup>b</sup>OM refers to organometallic precursor.